Development of a continuous process for EPDM devulcanization in an extruder

Sutanto, Poppy

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
1. Introduction

In this chapter, the engineering kinetic model derived in chapter 3 is applied to a continuous process. Figure 4.1 depicts the parameters that influence the devulcanization reaction studied in Chapter 3. All of them have positive influence on the devulcanization (conversion) rate, as has been shown by equations (2) and (3) in Chapter 3.

A self-wiping co-rotating extruder was used for this study. It is considered as a continuous reactor, modelled by stirred tank and plug flow reactors in series. The residence time is calculated based on the flow rate, the rotation speed of the screws and the back flow rate. By knowing the residence time of the material in the reactor and the shear rate applied to it in each screw section, the degree of conversion (degree of decrosslinking) can be calculated. The calculated crosslink densities of the material leaving the extruder were compared with the experimental ones to validate the model.

Figure 4.1. Parameters influencing the devulcanization reaction
2. Materials and Equipments

2.1. Materials

The EPDM compound used here was profile material; the same material was used in Chapter 3 to derive the engineering kinetic equations. Hexadecylamine from Acros and Sunpar 150 oil were used in the process.

The crosslink density was measured in decaline, and its value was calculated according to the Flory-Rehner equation [1].

2.2. Equipments

A co-rotating twin screw extruder from APV Baker with a length of 1.25 m and a screw diameter of 5 cm was used for this research.

The amine used in this research has a melting point above the room temperature (38-47°C). The Hexadecylamine is difficult to handle in its solid form due to its hygroscopicity and bad flowability. Earlier attempts to feed the amine into the extruder in its solid form did not succeed due to the poor flowing property of the powder.

Therefore, it was decided to feed the amine as a liquid, by preheating it in a jacketed vessel and pumping it as a melt into the extruder. A peristaltic pump equipped with Teflon tubing (isolated by a heating wire) is suitable for this purpose, while other type of pumps suffer from clogging problems with this amine.

3. Modelling Concept

Modelling of a process in the extruder is a matter of calculating the effects of all the extrusion parameters on the conversion. Figure 4.2 shows the initially suggested modelling scheme for the devulcanization process studied. Barrel temperature, screw configuration, feed rate, screw speed and die resistance are the control parameters, the values of which can be set. The other parameters in figure 4.2 are dependent directly or indirectly on the control ones.

In a numerical modelling procedure, the values of the dependent parameters can be calculated by dividing the extruder in smaller segments (for example 2.5 cm segments, as was chosen in the present case). The length of a segment is adjusted as a function of the reaction speed: a shorter segment for a faster reaction rate, and the other way around. Since the conversion within a segment is assumed to be very low, the structure of the material will not change drastically and hence its physical properties can be assumed as constant over each segment.

The physical properties of the material are determined amongst others by the degree of conversion, which is dependent on the reaction time, concentrations and process conditions (in this case temperature and shear rate). The phase of the material (solid/liquid), heat transfer coefficient, density, viscosity, heat capacity and friction coefficient between the rubber and the channel walls are the physical properties to be
considered. These are used in a segment for calculating the degree of conversion and, in turn, the physical properties of the succeeding segment.

Figure 4.2. Initial extruder modelling scheme (+:positive effect, -:negative effect)

The key of this modelling method is that all the physical properties must be measurable, which is unfortunately not the case in a devulcanization process. The main problems in determining the physical properties were encountered in the friction coefficient and viscosity measurement. The friction coefficient was difficult to measure, since the devulcanization process causes particle size modification and phase transition. The viscosity of the devulcanized rubber was hard to measure, especially at low degree of conversion and when the material is unstable (it recrosslinks during the measurement). During the devulcanization, the material is gaining back its fluidity. This transition is not sharp: when the rubber is not fully devulcanized, it consists of solid vulcanizate particles and devulcanizate melt. This in turn disturbs the viscosity measurement, giving instability during the test. Shortly, the viscosity term is only available after a certain degree of conversion is reached, which is not always the case when the feed rate, hence the residence time, is varied.

Due to the restrictions in the modelling system as presented in figure 4.2, a simpler method was proposed, considering the extruder as a series of shearing reactors. By calculating the shear rate of each screw type and the residence time in each reactor and inserting them in the model derived in Chapter 3, the degree of conversion (in terms of crosslink density and HDA concentration) can be calculated.

The new modelling scheme is depicted in Figure 4.3, with the parameters in the grey boxes as the control variables. Thus, the screw configuration, screw speed, the reaction temperature and feed rate are the control variables studied.
configuration, screw speed and feed rate altogether determine the residence time in the extruder. The shear rate is determined by the screw speed and screw geometry.

![Diagram of the modelling concept of the simplified extrusion model](image)

**Figure 4.3.** The modelling concept of the simplified extrusion model

### 4. Calculations of the parameters

From the kinetic model obtained from batch experiments, two parameters are necessary to be calculated in order to determine the final conversion, i.e. the residence time and the shear rate.

Before discussing the equations used in the extruder modelling, several assumptions are introduced:

1. Leakage flow is negligible, considering the high viscosity of rubber. In most part of the extruder, the EPDM is in solid phase as rubber crumbs, which turns into a highly viscous melt formed after devulcanization reaches a certain critical decrosslinking degree.

2. The whole extruder is divided into two sections: solid transport section and liquid flow section. The length of each section varies for each experiment, depending on the devulcanization rate at various experimental conditions. Table 4.1 shows the measured crosslink densities of the samples from batch experiments, at which points the rubber is macroscopically devulcanized. These numbers suggest that a minimum conversion of 65% is required for this material to be considered as liquid. Therefore, this conversion was chosen as the phase transformation point. The solid flow model is thus applied from the feeding point until the point where the decrosslinking degree is 65%, and the liquid flow model for the rest of the extruder length. The assumption of a critical degree of conversion is a common method in the kinetic-influenced rheology [2].
Table 4.1. Relative decrease in crosslink densities of the EPDM profile material from the batch experiment sample, when the rubber appears to be a liquid

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>rpm</th>
<th>reaction t(min)</th>
<th>Relative decrease in Xlink (experimental data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>225</td>
<td>90</td>
<td>15</td>
<td>67.6%</td>
</tr>
<tr>
<td>225</td>
<td>100</td>
<td>15</td>
<td>66.5%</td>
</tr>
<tr>
<td>225</td>
<td>110</td>
<td>15</td>
<td>68.3%</td>
</tr>
<tr>
<td>225</td>
<td>120</td>
<td>15</td>
<td>69.6%</td>
</tr>
</tbody>
</table>

3. Newtonian flow is assumed, since the exact flow behaviour during the devulcanization process is unknown. Newtonian flow was also assumed in the shear rate calculation in the Brabender when deriving the engineering kinetic model. Since it is important for the extrusion modelling to apply similar operating conditions as in the Brabender, taking the same assumption for the extrusion process seems reasonable.

Calculation for the extruder process was performed according to the procedure in Figure 4.4. In the screw sections where a plug flow was assumed, the calculation was done per segment of 2.5 cm by first calculating the residence time and shear rate in that section, and then introducing them into the kinetic model from Chapter 3 to obtain the degree of conversion. From the degree of conversion, the corresponding HDA concentration and crosslink density at the end of each segment were calculated. These values were taken as initial ones in the calculation for the succeeding segment. On the other hand, the conversion in the sections where continuous stirred tank reactor (CSTR) behaviour was assumed, was performed without dividing the section in segments (Figure 4.4).
Figure 4.4. Calculation procedure for modelling the conversion in the extruder

4.1. Shear rate

Shear rate is dependent on the screw geometry and rotation speed according to the following equations [3,4]:

1. For 90° kneading elements:

\[
\dot{\gamma} = 24.56 + 0.42 \cdot (10^6 Q - 0.005) - 0.072 \cdot \ln(2 \cdot 10^5 Q) \cdot (60N - 25) + 0.98 \cdot (60N - 25)
\]

(1)
2. For pressure build up elements:

\[
\dot{\gamma} = 4.8 N \cdot 10^4 \cdot Q
\]  

(2)

4.2. Residence time

The residence time of a material in a continuous reactor, can be simply calculated when the filled (effective) volume of the reactor \((V_R)\) and the flow rate \((Q)\) are known, according to:

\[
\tau = \frac{Q}{V_R}
\]  

(3)

and

\[
V_R = V \cdot f
\]  

(4)

where \(V\) is the reactor volume and \(f\) is the degree of fill.

The reactor volume is calculated for each screw type, using the following relation:

\[
V = A_l \cdot l
\]  

(5)

\(l\) is the length in the screw axial direction, while \(A_l\) is the cross-sectional area of the gap between the screw and the barrel [5,6] as depicted in figure 4.5 for the transporting elements:

\[
A_l = (k_b - 2k_s) \cdot R_s^2
\]  

(6)

\[
k_b = 2 \cdot (\pi - \psi) + \frac{C_L}{R_s} \cdot \sin \psi
\]  

(7)

\[
k_s = n \cdot \left[ \psi \cdot \left( \frac{C_L}{R_s} \right)^2 - \frac{C_L}{R_s} \cdot \sin \psi + \frac{\alpha}{2} \cdot \left( \frac{C_L}{R_s} \right)^2 - 2 \cdot \frac{C_L}{R_s} + 2 \right]
\]  

(8)

\[
\cos \psi = \frac{C_L}{2R_s}
\]  

(9)
Chapter 4: Continuous Devulcanization in an Extruder

Figure 4.5. cross section of a pair of corotating screws with 2 tips [6]

The degree of fill of the extruder is dependent on the screw configuration, feed rate and screw speed. In a transporting screw element, the degree of fill is calculated by:

\[ f = \frac{Q}{Q_{D,\text{max}}} \]  

(10)

4.2.1. Solid model

The rubber waste is added as rubber crumbs into the extruder by means of a hopper. The rubber crumbs behave as solid particles in the extruder; they do not adhere to the channel walls as in the case of viscous liquid transport and hence the gravitational force can play an important role.

The differences in solid flow model and liquid flow model are in the calculation of the volumetric flow rate \( Q \) and the maximum drag flow capacity \( Q_{D,\text{max}} \). For solid section, equation (3) becomes:

\[ t = \frac{Q}{V_R} = \frac{Q_{\text{solid}}}{V_{\text{section}} \cdot f} = \frac{Q_{\text{solid}}}{A_l \cdot dl \cdot f} \]  

(11)

where \( dl \) is the length of the segment (2.5 cm).

\( Q_{\text{solid}} \) is determined by the rubber feed rate and the density. Considering the rubber is in the solid phase, the volumetric flow rate of the rubber bed \( Q_{\text{solid}} \) was calculated using the bulk density of the rubber crumb (\( \rho_{\text{bulk}} \)):

\[ Q_{\text{solid}} = \frac{\dot{M}}{\rho_{\text{bulk}}} \]  

(12)
In order to calculate the degree of fill $f$ in equation (10), the maximum drag flow capacity $Q_D$ for solid section is calculated as:

$$Q_{D,\text{max}} = A_l \cdot v_l$$
$$Q_{D,\text{max}} = A_l \cdot t_s \cdot N$$

(13)

### 4.2.2. Liquid model

For the liquid section, equation (3) becomes:

$$t = \frac{Q}{V_R} = \frac{Q_{\text{liquid}}}{V_{\text{section}} \cdot f} = \frac{Q_{\text{liquid}}}{A_l \cdot dl \cdot f}$$

(14)

The volumetric rubber flow rate $Q_{\text{liquid}}$ is calculated using the density of the rubber:

$$Q_{\text{liquid}} = \frac{\dot{M}}{\rho_{\text{rubber}}}$$

(15)

The degree of fill in equation (10) is calculated by using the maximum drag capacity for liquid flow:

$$Q_{D,\text{max}} = 0.5m \cdot H \cdot W \cdot V_z \cdot f_D$$

(16)

$$V_z = \pi \cdot N \cdot D_s \cdot \cos \varphi$$

(17)

$$\varphi = \tan^{-1}\left(\frac{t_s}{2\pi R_s}\right)$$

(18)

$H$ is the height of the channel, $W$ is the width of the channel, $t_s$ is the screw thread, $m$ is the number of parallel channels, calculated using the following equation [6]:

$$m = 2 \cdot n_s - 1 + \frac{\alpha \cdot n_s}{\pi}$$

(19)

with $n_s$ as the number of screws, and $\alpha$ the tip angle in radians. The $f_D$ in equation (16) is the geometrical correction factor for drag flow, calculated numerically using the method described by Booy [6]. The drag flow coefficient is necessary to correct the volume of the screw channel due to its curvature.

Kneading sections with 90° stagger angle and -45° stagger angle (which are applied in this research) have no positive pumping action and therefore their degree of fill is always 1. The material is pushed through these sections by the preceding pressure build up elements.

At the end of the pumping zone at the extruder exit, the die provides resistance to the flow according to equation (20); therefore, backflow occurs in this last zone.

$$\Delta P_{\text{die}} = 4 \cdot \mu \cdot \dot{\gamma}_{\text{die}} \cdot \frac{L_{\text{die}}}{D_{\text{die}}^2}$$

(20)

and the shear rate is calculated according to equation (21)

$$\dot{\gamma}_{\text{die}} = 32 \cdot \frac{Q}{\pi D_{\text{die}}^3}$$

(21)
The presence of back flow \( (Q_p) \) increases the degree of fill by reducing the pumping capacity of the screw, according to:

\[ Q = Q_D - Q_p \]  

(22)

The pressure drop \( (dp/dz) \) in the down-channel direction is calculated from the back flow by:

\[ \frac{dp}{dz} = Q_p \cdot \frac{12 \cdot \mu}{m \cdot W \cdot H^3 \cdot f_p} \]  

(23)

The \( f_p \) is the geometrical correction factor for pressure flow, calculated using the method described by Booy [6]. The length of fully filled part is calculated as follow:

\[ Z_{ff} = \frac{\Delta P_{die}}{dp/dz} \]  

(24)

The degree of fill of the screw zone is:

\[ f = \frac{Z_{ff}}{Z_{zone}} + \left(1 - \frac{Z_{ff}}{Z_{zone}}\right) \cdot \frac{Q}{Q_D} \]  

(25)

![Figure 4.6](image)

Figure 4.6 z is the down-channel direction and l is the direction along the screw axis.

Since the pressure drop is calculated in down-channel direction z (see figure 4.6), the degree of fill is also calculated in the same direction by converting the length of the pumping zone to the l (screw axial) direction:

\[ Z_{zone} = \frac{l_{zone \ in \ l \ direction}}{\sin \phi} \]  

(26)

The residence time in this pumping zone is then calculated by substituting equation (26) into equation (4) and subsequently equation (3). Therefore, the residence time is increased by the occurrence of back flow.
4.3. Conversion

The conversion is calculated in the flow direction, from the inlet point and to the exit point. The calculation is done per segment as a function of the residence time and the shear rate in the corresponding section, using equations (1-3) and the parameters in table 3.2 of Chapter 3. The resulting crosslink density and HDA concentration are used for the calculation of the succeeding section.

\[
-r_{Xlink} = -\frac{d[Xlink]}{dt} = k_1(T, \dot{\gamma}) \cdot [Xlink]^a [HDA]^b + k_2(T, \dot{\gamma}) \cdot [Xlink]^c
\]  
\[ (27) \]

\[
-r_{HDA} = -\frac{d[HDA]}{dt} = k_3(T, \dot{\gamma}) \cdot [Xlink]^a [HDA]^b + k_4(T, \dot{\gamma}) \cdot [HDA]^d
\]  
\[ (28) \]

The extruder is considered as a series of CSTR’s and PFR’s. The screw sections where backflow occurs, namely in the mixing section (+45° followed by -45° stagger angle) and in the pumping zone before the die, are considered as a number of CSTR’s and conversion is calculated directly for the whole section, while the rest of the extruder is considered as a PFR where calculation is done per segment. Mass balance equations derived for steady state reactors [7], where the accumulation in the reactor is zero, are applied and rearranged into the following equations:

1. The conversion in a plug flow section is calculated using equations (29) and (30) by solving them simultaneously (and numerically):

\[
t = -\int \frac{[Xlink]}{r_{Xlink}} \frac{d[Xlink]}{dt}
\]  
\[ (29) \]

\[
t = -\int \frac{[HDA]}{r_{HDA}} \frac{d[HDA]}{dt}
\]  
\[ (30) \]

2. The conversion in a CSTR is calculated using equations (31)-(32). This calculation assumes that the outgoing HDA concentration and crosslink density are equal to the concentration inside the reactor.

\[
t = \frac{[Xlink]_i - [Xlink]_o}{-r_{Xlink}}
\]  
\[ (31) \]

\[
t = \frac{[HDA]_i - [HDA]_o}{-r_{HDA}}
\]  
\[ (32) \]
5. Experimental procedures

5.1. Simulation of the effects of Screw Design, Flow Rate, and Rotation Speed on the Residence Time

From equations (29)-(32) it is obvious that the residence time plays an important role in the degree of conversion. Residence time in the extruder is influenced by screw configuration, screw speed and throughput. Since changing the screw configuration is not a convenient method to vary the residence time, the screw configuration is simulated in the beginning to find the one that can provide the longest residence time. This configuration was then used for the rest of experiments. Variation of residence time between the experiments could be done by varying the throughput and the screw speed.

5.1.1. Finding the proper screw configuration (modelling residence time vs. screw configuration)

Residence time in the extruder can be increased by using more screws with smaller pitch angle, i.e. smaller transporting capacity. Kneading elements at 90° stagger angle do not have transport capacity. The material passing these kneading elements is pushed in the down channel direction by the preceding transport element. Therefore, the length of the kneading sections should not be too long in order to prevent too high torque, which will disturb the extruder operation.

For the purpose of designing the screw configuration, the problem was simplified into transport of rubber material without taking into account the conversion, phase transformation and backflow.

Simulation has been done in order to compare the residence time obtained by several screw configurations, as depicted in Figure 4.7. The filled volume was calculated using equations (4)-(6) and (14), while the estimated residence time (at 5 kg/h throughput and 25 rpm screw speed) was calculated using equation (3). The results of the residence time simulation are shown in Table 4.2.
Table 4.2. Filled volume of the extruder vs. screw configuration

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Filled volume (m³)</th>
<th>Residence time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0.6 m TE + 0.4 PBU + 0.25 m KE</td>
<td>4.48E-4</td>
<td>323</td>
</tr>
<tr>
<td>2 0.5 m TE + 0.5 m PBU + 0.25 m KE</td>
<td>4.88E-4</td>
<td>352</td>
</tr>
<tr>
<td>3 0.325 m TE + 0.675 m PBU + 0.25 m KE</td>
<td>4.78E-4</td>
<td>344</td>
</tr>
<tr>
<td>4 0.325 m TE + 0.575 m PBU + 0.35 m KE</td>
<td>5.95E-4</td>
<td>428</td>
</tr>
<tr>
<td>5 0.325 m TE + 0.525 m PBU + 0.4 m KE</td>
<td>6.54E-4</td>
<td>471</td>
</tr>
<tr>
<td>6 0.225 m TE + 0.525 m PBU + 0.5 m KE</td>
<td>6.65E-4</td>
<td>478</td>
</tr>
</tbody>
</table>

Since the devulcanization proceeds slowly, configuration 6 was chosen for the extruder experiments due to its longest residence time. The resulting extruder setup can be seen in figure 4.8. The kneading sections with 90° stagger angle were spread along the extruder, with pressure build up elements between them to provide pushing action on the material to pass the non-transporting kneading sections.
5.1.2. The influence of screw speed and throughput on the residence time

The following simulations were made to give an idea how large the influences (of the screw speed and throughput) are on the residence time. The effect of screw speed on the residence time, at a constant flow rate of 5 kg/h using screw configuration 6, is depicted in figure 4.9. The variation in the residence time with the screw speed is small, i.e. of maximum 20%, in the working range of 25-200 rpm. Simulation on the effect of throughput on the residence time was made at a rotation speed of 25 rpm, using screw configuration 6.
In contrast with the screw speed, the effect of throughput on the residence time is much more significant, as depicted in figure 4.10. Varying the throughput between 2 and 20 kg/h results in residence time variation of 18 to 3 minutes.

![Figure 4.10. Residence time as a function of throughput in the extruder](image)

5.2. Experimental Scheme

Experiments in the extruder were carried out by varying the rotation speed, rubber flow rate, and barrel temperature. The rotation speed was varied between 50-200 rpm, set temperature between 250-300°C, HDA concentration of $3 \times 10^{-4}$ mol/g rubber compound and rubber flow rate 3-7 kg/h.

6. Results and Discussions

6.1. Viscosity of the devulcanizate

In a common modelling procedure for reactive polymer processing, the viscosity ($\mu$) is used as an indication of the extent of the reaction and the value is calculated as a function of shear, temperature and molecular weight. The devulcanization reaction involves a phase transition, from solid rubber crumbs into melt. The fact that this phase transition is a result of the reaction complicates the viscosity modelling even more. The viscosity can only be measured (still very roughly) after a certain degree of decrosslinking is reached, the point where the rubber starts to flow.

The apparent viscosity values in this research were approximated by measuring the die pressure at various flow rates and using them in equations (20) and (21). The viscosity values found from the experiments were not accurate due to the presence of 2 phases in the devulcanizate (solid rubber crumb with viscous devulcanizate) as can be
seen in Figure 4.11. Figure 4.11(a) shows the plot of the apparent viscosity against the shear rate, at different temperatures. The plot shows a negligible effect of shear rate on the apparent viscosity values; this in turn supports the Newtonian flow assumption taken. Figure 4.11(b) shows a more significant dependency of the apparent viscosity values on the degree of conversion (represented by the measured crosslink density), although the spread is still too wide to derive an appropriate model.

As it has been observed during the modelling, the viscosity term apparently does not have significant influence in the degree of fill. Substituting equations (20) and (22) in equation (23), the viscosity terms are eliminated. In practice, viscosity variation might take place in the screw zones and hence will influence the pressure build up profile due to the non-isoviscous flow (equations (23) and (24)). This viscosity variation might occur due to the difference in the temperature profile, degree of conversion, and non-Newtonian flow.

![Figure 4.11 Apparent viscosity: (a) as a function of shear rate, and (b) as a function of [crosslink]](image)

6.2. Degree of conversion model vs. degree of conversion experimental data

The result of the extrusion modeling is presented in figure 4.12; the predicted decrosslinking degrees are plotted against the measured ones from the experiments within the range of temperature in the batch experiments (225-285°C set temperature) at shear rate of 50-217 s⁻¹, respectively). The crosslink density is measured in decaline, using the same method as discussed in Chapter 3 and the corresponding decrosslinking degree is calculated as:

\[
\text{Decrosslinking degree} = \frac{XL_0 - XL_{end}}{XL_0} \times 100\%
\]  

(33)

The result shows a good agreement, giving a standard error of 3.5%. The standard error of estimate is defined as [8]
Chapter 4: Continuous Devulcanization in an Extruder

\[
\text{Standard Error} = \sqrt{\frac{\sum (\text{Decrosslinking degree}_{\text{exp}} - \text{Decrosslinking degree}_{\text{model}})^2}{n_{\text{exp}} - 2}} \quad (34)
\]

with \( n_{\text{exp}} \) as the number of experiments.

Unfortunately, when the kinetic model was applied to an extended set temperature (300°C), the measured conversions are much higher than the predicted values (see figure 4.13). This is likely due to the significant degradation, which was not observed in the batch experiments due to the limitation in the Brabender operating temperature. Degradation is more likely to occur at higher temperature, resulting in main chain breakage and therefore in lower values of the measured crosslink density. Analysis in the GPC (figure 4.14) of a devulcanizate from an experiment at 300°C set temperature, 50 rpm, and 3.5 kg/h rubber feed rate shows a decrease of MW to half of its original value (23 000 vs. 58 000 g/mol, respectively). The measured crosslink density of this sample is \( 6.1 \cdot 10^{-5} \) mol/g rubber, compared to its predicted value of \( 1.2 \cdot 10^{-4} \) mol/g rubber. Although it is tempting to draw a conclusion that the 100% difference in the crosslink density measured is caused by the 50% decrease of the average MW, a more quantitative approach, which is outside the scope of this research, would be needed to completely explain this.
7. Conclusions

Modelling a devulcanization process in an extruder needs a number of simplifications due to the unavailability of physical properties data, especially the viscosity. Considering the simplifications and assumptions used here, it is fair to say that the model can predict the conversion in the extruder quite satisfactorily.

Extrapolating the experimental conditions to a higher temperature did not give a good agreement, due to the occurrence of phenomena that were not observed when deriving the engineering kinetic model. However, these observed deviation can be
easily, although only qualitatively, explained by taking into consideration the degradation of the rubber at high temperature.

The analysis on the devulcanizate does not show any significant amount of degradation product. The average molecular weight of the devulcanizate extract is around 40% lower than that of the virgin material, suggesting that there is less than one scission per polymer chain of the sol fraction.

The successful continuous devulcanization process modelling shows that the extruder operating conditions can resemble the operating conditions in the batch system to attain the same shear and residence time.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL</td>
<td>centerline distance between the screw axes</td>
<td>m</td>
</tr>
<tr>
<td>F</td>
<td>degree of fill</td>
<td>-</td>
</tr>
<tr>
<td>f_D</td>
<td>geometrical correction factor for drag flow</td>
<td>-</td>
</tr>
<tr>
<td>f_P</td>
<td>geometrical correction factor for pressure flow</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>height of the channel</td>
<td>m</td>
</tr>
<tr>
<td>[HDA]</td>
<td>concentration of HDA in the rubber</td>
<td>mol HDA/g rubber</td>
</tr>
<tr>
<td>l</td>
<td>length in the screw axis direction</td>
<td>m</td>
</tr>
<tr>
<td>L</td>
<td>total extruder length</td>
<td>m</td>
</tr>
<tr>
<td>M</td>
<td>number of parallel channels</td>
<td>-</td>
</tr>
<tr>
<td>M</td>
<td>mass flow rate</td>
<td>kg/s</td>
</tr>
<tr>
<td>n</td>
<td>number of screw tips</td>
<td>-</td>
</tr>
<tr>
<td>N</td>
<td>rotation speed</td>
<td>rps</td>
</tr>
<tr>
<td>Q</td>
<td>volumetric flow rate</td>
<td>m³/s</td>
</tr>
<tr>
<td>Q_D,max</td>
<td>maximum drag flow capacity</td>
<td>m³/s</td>
</tr>
<tr>
<td>R_s</td>
<td>outside radius of the screw</td>
<td>m</td>
</tr>
<tr>
<td>R_B</td>
<td>barrel radius</td>
<td>m</td>
</tr>
<tr>
<td>T</td>
<td>residence time</td>
<td>s</td>
</tr>
<tr>
<td>t_s</td>
<td>screw lead</td>
<td>m</td>
</tr>
<tr>
<td>V</td>
<td>reactor volume</td>
<td>m³</td>
</tr>
<tr>
<td>V_R</td>
<td>filled reactor volume</td>
<td>m³</td>
</tr>
<tr>
<td>W</td>
<td>width of the channel</td>
<td>m</td>
</tr>
<tr>
<td>[Xlink]</td>
<td>crosslink density</td>
<td>mol/g rubber</td>
</tr>
<tr>
<td>γ</td>
<td>shear rate</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>φ</td>
<td>helix angle at R_s</td>
<td>rad</td>
</tr>
<tr>
<td>μ</td>
<td>viscosity</td>
<td>Pa.s</td>
</tr>
<tr>
<td>T</td>
<td>shear stress</td>
<td>Pa</td>
</tr>
</tbody>
</table>
References